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(21)Application number : **2001-362069**(71)Applicant : **SHIONOGI & CO LTD**(22)Date of filing : **28.11.2001**(72)Inventor : **HAMANO HIDEAKI
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(30)Priority

Priority number : **2000363211** Priority date : **29.11.2000** Priority country : **JP****(54) SILICA CARRIER FOR AGRICULTURAL FORMULATION AND AGRICULTURAL FORMULATION**

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a solid formulation having excellent preservation stability of a fine powder and a granular wettable powder having excellent disintegrating properties due to high water dispersibility and slight occurrence of aggregation because the silica carrier has the characteristic values.

SOLUTION: The silica carrier for the agricultural formulation is characterized in that the carrier is an amorphous silica having the definite pore peak of $\geq 100 \text{ mm}^3/\text{nm.g}$ maximum dV_p/dR_p (wherein, R_p denotes the pore radius; V_p denotes the pore volume) and 1-20 nm pore peak radius.

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CLAIMS

[Claim(s)]

[Claim 1] Silica support for agricultural-chemicals pharmaceutical preparation which the maximum dVp/dRp (however, Rp shows a pore radius and **** shows pore volume) has a clear pore peak more than 100mm³/nm-g, and is characterized by a pore peak radius being 1-20nm by amorphous silica.

[Claim 2] Agricultural-chemicals pharmaceutical preparation containing silica support according to claim 1.

[Claim 3] Agricultural-chemicals solid preparations containing silica support according to claim 1.

[Claim 4] Agricultural-chemicals granulation water dispersible powder containing silica support according to claim 1.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the silica support for agricultural-chemicals pharmaceutical preparation, and agricultural-chemicals pharmaceutical preparation.

[0002]

[Description of the Prior Art] Conventionally, in the field of agricultural-chemicals pharmaceutical preparation, the sedimentation nature silica which is a kind of amorphous silica has been widely used as support. The application is used for **, such as adsorbents, such as a grinding aid, a fluid improvement agent of a solid preparation, a solvent, and an agricultural-chemicals liquid Hara object, and the various purpose. As dosage forms, although mainly used with solid preparations, when a solid original object was formed into after [grinding] liquids and solutions by dry type, it might be used also for liquids and solutions. However, a sedimentation nature silica does not have the clear shape of particle, and is hurt ** quantity, and it may be easy to change the gestalt of a particle by the stimulus from the outside, such as force and temperature, and may condense, or it may solidify massive. In powder pharmaceutical preparation, such as the result, for example, powder material, and water dispersible powder, it had the trouble that the liquid component which was being made to support during preservation oozed out, or caking by superfluous adhesion of sedimentation nature silicas arose. Furthermore, when there were many contents of a sedimentation nature silica like a granule, granulation water dispersible powder, and an application-on-water-surface agent in the case of the pharmaceutical preparation of the shape of granular or a tablet, even if it could fabricate, underwater collapsibility was very bad [it could blockade and could not fabricate by the granulation inside of a plane, and]. In the case of the pharmaceutical preparation of the making it distribute underwater like granulation water dispersible powder or an application-on-water-surface agent especially purpose, underwater collapsibility and dispersibility were important physical properties, and it was difficult to make the pharmaceutical preparation which has good physical properties using a sedimentation nature silica. Agricultural-chemicals Hara objects were a liquid and a semisolid, and when viscous, the fault of a sedimentation nature silica especially increased.

[0003] in this case, using the burned product of such a wet silica as support is proposed -- **** (the patent No. 2976496 official report) -- in addition, it was inferior to dispersibility, and there was little what has the physical properties which were excellent as support for agricultural chemicals by current, and development of a good silica the preservation stability of agricultural chemicals and water-dispersion was desired.

[0004] It was made in order that this invention might meet the above-mentioned request, and it aims at offering the silica support for agricultural-chemicals pharmaceutical preparation with water-dispersion [preservation stability or water-dispersion / very high] and agricultural-chemicals pharmaceutical preparation of agricultural chemicals.

[0005]

[The means for solving a technical problem and the gestalt of implementation of invention] In order that this invention person may attain the above-mentioned purpose, as a result of inquiring wholeheartedly dVp/dRp By (however, Rp shows a pore radius's and **** shows pore volume's) having a clear pore peak more than 100mm³/nm-g, and using the amorphous silica whose pore peak radius is 1-20nm as silica support for agricultural-chemicals pharmaceutical preparation Caking after preservation is improved, and water-dispersion is very good, and carries out the knowledge of the ability to offer the agricultural-chemicals pharmaceutical preparation excellent in the homogeneity diffusibility of an active principle, and it came to make this invention.

[0006] Hereafter, lessons is taken from this invention and it explains in more detail. Maximum dVp/dRp has a clear

pore peak more than 100mm³/nm-g, and the silica support for agricultural-chemicals pharmaceutical preparation of this invention is amorphous silica whose pore peak radius is 1-20nm. Here, Rp shows a pore radius and **** shows pore volume.

[0007] In addition, in this invention, specific surface area, pore volume, pore distribution, and a pore peak radius are the values computed from the nitrogen adsorption process, and are the value computed from the following detailed approaches.

[0008] [Specific surface area] Using the full automatic specific surface area made from Japanese Bell / pore distribution measuring device (BELSORP28), the adsorption isotherm of nitrogen gas is measured and the sample which carried out the vacuum deairing for 90 minutes at 160 degrees C is computed from a BET adsorption method (bibliography: S.Brunauer, P.H.Emmett, E.Teller, J.Amer.Chem.Soc., 60,309 (1938)).

[0009] [Pore volume] Based on JIS-K1150, pore volume is computed with the analysis method of a DORIMOA heel at 160 degrees C from the nitrogen desorption constant-temperature line which measured the sample which carried out the vacuum deairing for 90 minutes by the above-mentioned BELSORP28. In addition, the range of the pore radius which computes pore volume is 1-100nm.

[0010] [Pore distribution] Pore distribution is searched for from the nitrogen desorption constant-temperature line which measured the sample which carried out the vacuum deairing for 90 minutes at 160 degrees C by the above-mentioned BELSORP28. count of pore distribution -- approach [of a DORIMOA heel -- D. -- it analyzes by Dollimore, G.R.Heal, J.Appl.Chem., and 14.109(1964)].

[0011] From a [pore peak and pore peak radius] pore distribution curve, make into a pore peak the place which shows the maximum of dVp/dRp, and let the radius in the peak be a pore peak radius.

[0012] it mentioned above from setting to the silica of this invention, and a structure top and the physical properties of what has maximum dVp/dRp smaller than 100mm³/nm-g being equivalent to the usual sedimentation nature silica, the adhesion of silicas being high, and water-dispersion falling -- as -- more than 100mm³/nm-g -- desirable -- 100-500mm³/nm-g -- more -- desirable -- 100-200mm³/nm-g -- it is 120-180mm³/nm-g still more preferably. Moreover, 1-20nm of 8-15nm of pore peak radii is 10-14nm still more preferably preferably. The measuring range in this approach is more than pore peak 1nm, and 1nm or less cannot be measured as mentioned above. If it exceeds 20nm, it will become very difficult for maximum dVp/dRp to obtain the silica more than 100mm³/nm-g. Moreover, when carrying out oil absorption, a thing 8nm or more has a pore peak radius desirable [a liquid Hara object, a semisolid Hara object, or a solvent] since oil absorption falls that a pore peak radius is less than 8nm and the absorptivity of an agricultural-chemicals liquid Hara object falls.

[0013] Furthermore, although the mean particle diameter of the silica of this invention is not specified especially, it is usually a 1-30-micrometer thing preferably 1 micrometers or more that what is necessary is just to grind at a pharmaceutical preparation process. If a less than 1-micrometer particle is too fine, and manufacture is difficult in the usual grinding classification facility and a particle is too coarse, homogeneity mixing with other components will become difficult at the time of agricultural-chemicals pharmaceutical preparation. However, in an agricultural-chemicals machine's for pharmaceutical manufacturing being fully capable as mentioned above, mean particle diameter does not become a problem.

[0014] Moreover, when using a liquid Hara object, a semisolid Hara object, or a solvent like for the purpose which mentioned above the silica used by this invention and which carries out oil absorption, the one where oil absorption ability is higher is desirable, and 150mL(s) / thing 100g or more has desirable DBP oil absorption. Although especially the upper limit is not restricted, it is usually 500mL(s) / 100g, and especially even if it exceeds this, it does not interfere.

[0015] In addition, as for the specific surface area (nitrogen adsorption process) by the BET adsorption method of this invention silica, it is especially desirable 200-500m²/g and that it is 200-250m²/g.

[0016] The silica of this invention can be obtained by the well-known approach according to the so-called process of the wet method silica to which alkali-metal silicate water solutions, such as a sodium silicate, and mineral acids, such as a sulfuric acid and a hydrochloric acid, are made to react.

[0017] the place by which it is characterized [the] -- the silicic-acid concentration in an alkali-metal silicate water solution -- 20 -- w/v % or less is less than [10 w/v%] preferably.

[0018] As a silicate, although a No. 3 sodium silicate is used from an economical standpoint in many cases, other

silicates can also be manufactured. Moreover, especially as a mineral acid, although neither carbonic acid nor phosphoric acid is specified, a sulfuric acid and a hydrochloric acid are well used from an economical standpoint. The concentration of a mineral acid has six to 16 desirable convention.

[0019] As a concrete manufacturing method, for example, the above-mentioned alkali-metal silicate water solution is warmed, and the sulfuric acid of predetermined concentration is added. The alkali-metal silicate water-solution temperature at the time of sulfuric-acid addition has good 40 degrees C or more, and it is 50-100 degrees C preferably. If needed, a sulfuric acid may be divided into several times and you may add. As a sulfuric-acid addition, the last neutralization index is 80 - 95% preferably 70% or more. What is necessary is just to heat after addition termination of a sulfuric acid if needed. Moreover, when a crystal cannot deposit easily, a salt like sodium sulfate may be mixed.

[0020] Although what is necessary is just to unite pH at the time of reaction termination with the target last pH, lowering to 5.5 or less is desirable.

[0021] The obtained silica slurry filters and washes this and re-distributes it in water. At this time, it is good to adjust pH to desired value again. Desired value can be doubled with the stability of an agricultural-chemicals active principle, and can be freely adjusted from weak acid to a weak base. Then, it filters, washes and dries and the silica of coarse grain is obtained. Furthermore, the silica of a predetermined grain size is obtained by grinding and the classification.

[0022] When using the above-mentioned silica as support for agricultural chemicals, this silica is mixed with an agricultural-chemicals Hara object, and it can apply [no] to well-known and used dosage forms, and is specified especially. And in the field for which the conventional sedimentation nature silica is used, it is usable satisfactory. For example, liquid pharmaceutical preparation, such as emulsification like homogeneity solution-like pharmaceutical preparation, such as solid preparations, such as granular pharmaceutical preparation, such as fines-like pharmaceutical preparation, such as powder material and water dispersible powder, a granule, a powder agent, and granulation water dispersible powder, and a tablet, or liquids and solutions, oils, an emulsifier, and a microemulsion agent, underwater suspension, the suspension in an oil, an underwater emulsion agent, the emulsion agent in an oil, and a microcapsule agent or letter pharmaceutical preparation of suspension, is mentioned. Each pharmaceutical preparation can be manufactured according to a well-known constituent and a well-known manufacturing method.

[0023] Usually, although the class and constituent of the agricultural-chemicals pharmaceutical preparation used were summarized into Table 1 below, it is not necessarily limited to these, and although the semi- component used by the class of agricultural-chemicals active principle, the purpose of using pharmaceutical preparation, and the using method an indispensable component and if needed may not necessarily be in agreement with the value of front Naka, it is usually following presentation within the limits, and is used. In addition, each % shows weight %.

[0024].

[Table 1]

製剤の種類	必須成分	準成分
油剤	農薬原体 (0.1~60%)、溶剤 (40~99.9%)	粘度調節剤 (40%以下)
乳化剤	農薬原体 (1~95%)、溶剤 (0.1~98%)、 界面活性剤 (1~40%)	
液剤	農薬原体 (1~80%)、水 (20~99%)	着色剤 (5%以下)、凍結防止剤 (20%以下)
マイクロエマルジョン剤	農薬原体 (0.1~70%)、水 (5~90%)、 界面活性剤 (1~50%)	防霉剤 (5%以下)、安定化剤 (5%以下)、 凍結防止剤 (20%以下)
水中エマルジョン剤	農薬原体 (1~50%)、水 (20~95%)、 界面活性剤 (0.1~30%)	増粘剤 (20%以下)、防霉剤 (5%以下)、 溶剤 (40%以下)、比重調節剤 (40%以下)、 凍結防止剤 (20%以下)、消泡剤(3%以下)
水中懸濁剤	農薬原体 (0.1~75%)、水 (10~95%)、 界面活性剤 (0.1~30%)	増粘剤 (20%以下)、防霉剤 (5%以下)、 溶剤 (40%以下)、比重調節剤 (40%以下)、 消泡剤(3%以下)
マイクロカプセル剤	農薬原体 (0.1~40%)、水 (20~95%)、 界面活性剤 (0.1~30%)、重合性モノマー (0.1~40%)	増粘剤 (20%以下)、防霉剤 (5%以下)、 溶剤 (40%以下)、比重調節剤 (40%以下)、 消泡剤(3%以下)
水中乳濁剤	農薬原体 (0.1~70%)、水 (10~95%)、 界面活性剤 (0.1~30%)	増粘剤 (20%以下)、防霉剤 (5%以下)、 溶剤 (40%以下)、比重調節剤 (40%以下)、 消泡剤(3%以下)
油中エマルジョン剤	農薬原体 (1~50%)、溶剤 (20~95%)、 界面活性剤 (0.1~30%)	増粘剤 (30%以下)、比重調節剤 (40%以下)、 (水)
油中懸濁剤	農薬原体 (0.1~75%)、溶剤 (10~95%)、 界面活性剤 (0.1~40%)	増粘剤 (30%以下)、比重調節剤 (40%以下)
粉剤	農薬原体 (0.1~95%)、固体担体 (0.1~99.9%)	ドリフト防止剤 (20%以下)、溶剤 (50%以下)、 流動性改善剤 (30%以下)、界面活性剤 (30%以下)、 吸油剤 (90%以下)
水溶剤	農薬原体 (0.1~95%)、水溶性担体 (0.1~99.9%)	界面活性剤 (40%以下)、消泡剤(3%以下)、 水溶性溶剤 (40%以下)、流動性改善剤 (30%以下)、 吸油剤 (90%以下)
水和剤	農薬原体 (0.1~95%)、固体担体 (0.1~98%)、 界面活性剤 (1~20%)	溶剤 (40%以下)、吸油剤 (60%以下)、 消泡剤(3%以下)、流動性改善剤 (30%以下)、
粉粒剤	農薬原体 (0.1~80%)、固体担体 (5~99%)	溶剤 (40%以下)、固結剤 (40%以下)、 界面活性剤 (40%以下)、
粒剤	農薬原体 (0.1~90%)、固体担体 (0.1~97%)、 界面活性剤 (0.1~10%)	溶剤 (50%以下)、固結剤 (40%以下)
顆粒水和剤	農薬原体 (0.1~90%)、固体担体 (0.1~97%)、 界面活性剤 (0.1~40%)	滑沢剤 (7%以下)、崩壊剤 (30%以下)、 固結剤 (20%以下)、消泡剤(3%以下)
錠剤	農薬原体 (0.1~95%)、固体担体 (0.1~98%)	滑沢剤 (7%以下)、崩壊剤 (30%以下)、 固結剤 (20%以下)、発泡剤 (40%以下)、 界面活性剤 (30%以下)、消泡剤(3%以下)

[0025] Furthermore, empty powder (liquids and solutions, solid preparation), application-on-water-surface pharmaceutical preparation (granular pharmaceutical preparation, a tablet, liquids and solutions, etc.), a seed treatment agent, a box processing agent, etc. are mentioned from a use side other than these. However, they are the names attached from the use side, and these are classified into the dosage forms mentioned above fundamentally,

and according to the purpose, the active principle content in pharmaceutical preparation is adjusted, or, in the case of a water surface suspension agent, they contain the with a specific gravity of one or less extending agent according to the gestalt of liquids and solutions and a solid preparation also in an application-on-water-surface agent. Moreover, in a seed treatment agent, adhesion of drugs contains coloring agents, such as acid blue and Rhodamine B, in many cases so that intelligibly.

[0026] Moreover, the effect enhancement agent which consists of various surfactants, such as oil, such as stabilizing agents, such as pH regulators, such as mixture of coloring agents, such as acid blue and rhodamine B, an anti-oxidant, a light absorption agent, HALS and monochrome, and diisopropyl phosphate, alkali-metal way acid chloride, and alkaline-earth-metal way acid chloride, mineral oil, an isoparaffin oil, silicon oil, and vegetable oil, a spreader which added various surfactants to them and a silicone system surfactant, and the 4th class ammonium system surfactant, etc. can also be added irrespective of the class of pharmaceutical preparation if needed.

[0027] Although the application in the inside of the various dosage forms of this silica is various and it is not limited especially, it is usually used for the following applications. However, as a component name, it is only dealt with as a solid support in many cases.

[0028] For example, when in the case of solid-state pharmaceutical preparation an agricultural-chemicals Hara object is a solid-state, or it is used as a grinding aid, a fluid improvement agent, a dust explosion reduction agent, etc. as opposed to the assistant of other solid-state components and an agricultural-chemicals Hara object contains a solvent etc. in the time of a liquid or a semisolid, or pharmaceutical preparation, it is used as a original object, an adsorbent of a solvent, etc. Moreover, in the case of liquid pharmaceutical preparation, as for example, a viscosity modifier, as a fluid improvement agent of the formed element to mix, when mixing after grinding a formed element, it is used as a grinding aid, a fluid improvement agent, a dust explosion reduction agent, etc.

[0029] Although the component listed to below above is illustrated, it is not restricted to these.

[0030] physical as an agricultural-chemicals active principle -- as description, you may be any of the shape of a solid-state, a liquid, and a semisolid, and a use application is not restricted to this, either, although an insecticide, miticide, a germicide, a herbicide, a plant growth regulator, an insect growth control agent, etc. are mentioned. For example, the following compound can be mentioned and one sort or two sorts or more of mixture of isomers, such as those geometrical isomers and an optical isomer, can also be mentioned.

[0031] O and O-dimethyl O-(3-methyl-4-nitrophenyl) phosphorothioate, O and O-dimethyl O-(3-methyl-4-(methylthio) phenyl) phosphorothioate, O, O-diethyl O-2-isopropyl-6-methylpyrimidine-4-IRUHOSUHO thioate, O and O-diethyl O- 3, 5, and 6-TORIKURORO-2-pyridyl phosphorothioate -- O, S-dimethyl acetyl HOSUHORAMIDO thioate, S-2, 3-dihydro-5-methoxy-2-oxo-- 1, 3, and 4-thiadiazole-3-ylmethyl O, O-dimethylphosphorodithioate, O and O-diethyl S-2-ethyl thio ethyl phosphorodithioate, 2 and 2-dichloro vinyl dimethyl phosphate, O-ethyl O-4-(methylthio) phenyl S-propylphosphorodithioate, O-4-cyanophenyl O, O-dimethyl phosphorothioate, and 2-methoxy-4H- 1, 3, and a 2-benzodioxaphospholine-2-sulfide -- O and O-dimethyl S-(N-methyl carbamoyl methyl) dithiophosphate, Ethyl 2-dimethoxy phosphinothioyl thio (phenyl) acetate, Diethyl (dimethoxy phosphinothioyl thio) succinate, dimethyls 2 and 2, 2-TORIKURORO-1-hydroxyethyl phosphonate, S-3, 4-dihydro-4-oxo-- 1, 2, 3-benzotriazine-3-ylmethyl O, O-dimethylphosphorodithioate, Dimethyl-((E)-1-methyl-2-(methyl carbamoyl) vinyl) phosphate, O, O, O', and O'-tetraethyl - Organic phosphorus system compounds, such as S and S'-methylenebis (phosphorodithioate), O-2, and 6-dichloro-4-methylphenyl O and O-dimethyl phosphorothioate,

[0032] A 2-sec-buthylphenyl methyl carver mate, ethyl N-{2, 3-dihydro-2, and 2-dimethyl benzofuran-7-yloxy carbonyl (methyl) amino thio}-N-isopropyl-beta-ARANINETO, A 2-isopropoxy phenyl-N-methyl carver mate, 2, 3-dihydro - 2 2-dimethyl-7-benzo[b]furanyl N-dibutylamino thio-N-methyl carver mate, A 1-naphthyl-N-methyl carver mate, S-methyl-N-(methylcarbamoyloxy) thio aceto imidate, 2-(ethyl thiomethyl) phenylmethyl carver mate, a 2-methyl-2-(methylthio) propionaldehyde O-methyl carbamoyl oxime, Carver mate system compounds, such as N and N-dimethyl-2-methylcarbamoyloxy imino-2-(methylthio) acetamide, S-4-phenoxy butyl-N, and N-dimethyl thio carver mate,

[0033] A 2-(4-ethoxy phenyl)-2-methyl-1-(3-phenoxy benzyl) oxy-propane, (RS) -alpha-cyano-3-phenoxy benzyl (RS)-2-(4-chlorophenyl)-3-methyl butyrate, (S) -alpha-cyano-3-phenoxy (benzyl S)-2-(4-chlorophenyl)-3-methyl butyrate, (RS) The -alpha-cyano-3-phenoxy benzyls 2, 2, and 3, 3-tetramethyl cyclopropane carboxylate, (RS) -alpha-cyano-3-phenoxy benzyl (1RS) - cis- , transformer-3-(2 and 2-dichloro vinyl)-2 and 2-dimethyl cyclopropane carboxylate, 3-phenoxy benzyl (1RS)-cis- , transformer-3-(2 and 2-dichloro vinyl)-2 and 2-dimethyl cyclopropane carboxylate, (RS) -alpha-cyano-3-phenoxy benzyl (1RS, 3Z) - cis--3-(2-chloro - 3, 3, and 3-trifluoro prop-1-enyl)-2 and 2-dimethyl cyclopropane carboxylate, (S) -alpha-cyano-3-phenoxy benzyl (1R) - cis--3-(2 and 2-dibromo

vinyl)-2 and 2-dimethyl cyclopropane carboxylate, (RS) -alpha-cyano-3-phenoxy benzyl (RS) -2 and 2-dichloro-1-(4-ethoxy phenyl) cyclopropane carboxylate, alpha-cyano-3-phenoxy benzyl N-(2-chloro - alpha, alpha, and alpha-trifluoro-p-tolyl)-D-BARINETO, 2-methyl-3-phenyl benzyl (1RS, 3Z) - cis-3-(2-chloro - 3, 3, and 3-trifluoro-1-propenyl)-2 and 2-dimethyl cyclopropane carboxylate, A 2-(4-BUOMO difluoro methoxyphenyl)-2-methyl-1-(3-phenoxy benzyl) methyl propane, (S) -alpha-cyano-3-phenoxy benzyl (1R) - cis-3-(1, 2, 2, and 2-tetrabromo ethyl)-2 and 2-dimethyl cyclopropane carboxylate, (4-ethoxy phenyl)-{3-(4-fluoro-3-phenoxyphenyl) propyl} dimethylsilane, The 3-phenoxy benzyl (1R)-cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-propenyl) cyclopropane carboxylate, (RS)-alpha-cyano - 3-phenoxy benzyl (1R) The - cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-propenyl) cyclopropane carboxylate, 5-benzyl-3-furil methyl (1R) The - cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-propenyl) cyclopropane carboxylate, (S) - alpha-cyano-3-phenoxy benzyl (R [1], 3Z)-cis- (2 and 2-dimethyl-3-{3-oxo--3-(1, 1, 1, 3, 3, and 3-hexafluoro propyloxy) propenyl} cyclopropane carboxylate --) (RS) -alpha-cyano-4-fluoro-3-phenoxy benzyl 3-(2 and 2-dichloro vinyl)-2 and 2-dimethyl cyclopropane carboxylate, 2, 3, 5, 6-tetrafluoro-4-methylbenzyl (1RS, 3Z) - cis-3-(2-chloro - 3, 3, and 3-trifluoro-1-propenyl)-2 and 2-dimethyl cyclopropane carboxylate, 2, 3, 5, 6-tetrafluoro benzyl (1R) - transformer-3-(2 and 2-dichloro vinyl)-2 and 2-dimethyl cyclopropane carboxylate, 3, 4, 5, 6-tetrahydro phthalimidomethyl (1RS) The - cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-pro ** nil) cyclopropane carboxylate, (RS) -2-methyl-4-oxo--3-(2-propenyl)-2-cyclopentene-1-IRU (1RS) The - cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-pro ** nil) cyclopropane carboxylate, (S) -2-methyl-4-oxo--3-(2-propynyl)-2-cyclopentene-1-IRU (1R) The - cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-pro ** nil) cyclopropane carboxylate, (RS) -1-ethynyl-2-methyl-2-pentenyl (1R) The - cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-pro ** nil) cyclopropane carboxylate, 2, the 5-dioxo-3-(2-propynyl) imidazolidine-1-ylmethyl (1R)-cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-pro ** nil) cyclopropane carboxylate, The 5-(2-propynyl) furfuryl (1R)-cis- , transformer -2, 2-dimethyl-3-(2-methyl-1-pro ** nil) cyclopropane carboxylate, Pyrethroid system compounds, such as the 5-(2-propynyl) furfuryls 2, 2, and 3 and 3-tetramethyl cyclopropane carboxylate, N-phosphono methyl glycine and its salt permitted in agricultural-chemicals study, 4 - Phospho RIREITIDO amino acid system compounds, such as a hydroxymethyl HOSUFI noil-L-gay alanyl-L-alanine.

[0035] ON 5-methoxy-3-(2-methoxyphenyl)- 1, 3, and 4-OKISA diazole-2-(3H)- Isopropyl 4, a 4'-dibromo benzoate, 4-chlorophenyl 2, 4, 5-TORIKURORO phenyl sulfone, The S and S-6-methyl quinoxaline -2, 3-diyl dithio cull BONETO, A 2-(4-tert-butyl phenoxy) cyclohexyl PUROPI-2-IRUSURU fight, Screw {tris (2-methyl-2-phenylpropyl) Tin} oxide, (4RS, 5RS)-5-(4-chlorophenyl)-N-chloro hexyl-4-methyl-2-oxo-- 1, 3-thiazolidine-3-carboxamide, 3, 6-screw (2-chlorophenyl) - 1, 2, 4, 5-tetrazine, 2-tert-butyl-5-(4-tert-butyl benzyl thio)-4-chloro pyridazine-3(2H)-ON, tert-butyl (E)-4-[(1, 3-dimethyl-5-phenoxy pyrazole-4-IRU) methylene amino oxymethyl] benzoate, N-4-tert-butyl benzyl-4-chloro - The 3-ethyl-1-methyl-5-pyrazole carboxamide, tetra-NAKUUCHIN, JINAKUCHIN, TORINA cutin, 5-chloro-N-[2-{4 - 2-ethoxyethyl -2, 3-dimethyl phenoxy} ethyl]-6-ethyl pyrimidine-4-amine), MIRUBEME cutin, abamectin, IBAME cutin, Azadirachtin [AZAD], 5-methyl [1, 2, 4] triazolo [3 and 4-b] benzothiazole, Methyl 1-(butylcarbamoyl) benzimidazole-2-carver mate, 6-(3, 5-dichloro-4-methylphenyl)-3(2H)-pyridazinone, 1-(4-chloro phenoxy)-3 and 3-dimethyl-1-(1H- 1, 2, 4-triazole-1-IRU) butanone, (E) -4-chloro-2-(trifluoromethyl)-N-[1-(imidazole-1-IRU)-2-propoxy ethylidene] aniline, A 1-[N-propyl-N-[2-(2, 4, 6-trichlorophenoxy) ethyl] carbamoyl] imidazole, (E) -1-(4-chlorophenyl)-4 and 4-dimethyl -2 -(1H- 1, 2, 4-triazole-1-IRU)- 1-pentene-3-oar, 1-(4-chlorophenyl)-4 and 4-dimethyl-2-(1H- 1, 2, 4-triazole-1-IRU) pentane-3-oar, (E) -1-(2, 4-dichlorophenyl)-4 and 4-dimethyl -2 -(1H- 1, 2, 4-triazole-1-IRU)- 1-pentene-3-oar, 1-(2, 4-dichlorophenyl)-4 and 4-dimethyl-2-(1H- 1, 2, 4-triazole-1-IRU) pentane-3-oar, 4-[3-(4-tert-buthylphenyl)-2-methylpropyl]-2, 6-dimethyl morpholine, 2-(2, 4-dichlorophenyl)-1-(1H- 1, 2, 4-triazole-1-IRU) hexane-2-oar, O and O-diethyl O-2-kino KISARINIRU Phosphorothioate, O- (6-ethoxy-2-ethyl-4-pyrimidinyl) O and O-dimethyl Phosphorothioate, 2-diethylamino -5, 6-dimethylpyrimidin-4-IRU Dimethyl carver mate, 4-(2, 4-dichlorobenzoyl)-1, 3-dimethyl-5-pyrazolyl p-toluene sulfonate, 4-amino-6-(1 and 1-dimethyl ethyl)-3-methylthio - 1, 2, 4-triazine-5(4H)-ON, 2-chloro-N-[(4-methoxy-6-methyl-1,3,5-triazine-2-IRU) aminocarbonyl] benzenesulfonamide, 2-

methoxycarbonyl-N-[(4, 6-dimethoxy pyrimidine-2-IRU) aminocarbonyl] benzenesulfonamide, 2-methoxycarbonyl-N-[(4, 6-dimethylpyrimidin-2-IRU) aminocarbonyl] benzenesulfonamide, 2-methoxycarbonyl-N-[(4-methoxy-6-methyl-1,3,5-triazine-2-IRU) aminocarbonyl] benzenesulfonamide, 2-ethoxycarbonyl-N-[(4-chloro-6-methoxy pyrimidine-2-IRU) aminocarbonyl] benzenesulfonamide, 2-(2-chloroethoxy)-N-[(4-methoxy-6-methyl-1,3,5-triazine-2-IRU) aminocarbonyl] benzenesulfonamide, A 2-methoxycarbonyl-N-[(4, 6-dimethoxy pyrimidine-2-IRU) aminocarbonyl] phenylmethane sulfonamide, A 2-methoxycarbonyl-N-[(4-methoxy-6-methyl-1,3,5-triazine-2-IRU) aminocarbonyl] thiophene-3-sulfonamide, A 4-ethoxycarbonyl-N-[(4, 6-dimethoxy pyrimidine-2-IRU) aminocarbonyl]-1-methyl pyrazole-5-sulfonamide, A 2-[4 and 5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo--1H-imidazole-2-IRU]-3-quinoline carboxylic acid, 5-ethyl -5, a [8-dihydro-8-oxo-[1, 3] JIOKISORO [4 and 5-] g] quinoline-7-carboxylic acid, 2-[4 and 5-dihydro-4-methyl-4-(1-methylethyl)-5-oxo--1H-imidazole-2-IRU]-5-ethyl-3-pyridinecarboxylic acid, Methyl 6-(4-isopropyl - 4-methyl-5-oxo-imidazoline-2-IRU)-m-toluate, Methyl 2-(4-isopropyl - 4-methyl-5-oxo-imidazoline-2-IRU)-p-toluate, 2-(4-isopropyl - 4-methyl-5-oxo-imidazoline-2-IRU) nicotinic acid, N-(4-chlorophenyl) methyl-N-cyclopentyl-N'-phenyl urea, (RS) -2-cyano-N-[(R) -1 (2, 4-dichlorophenyl) ethyl]-3 and 3-dimethyl butyl amide -- N-(1, 3-dihydro - 1, 1, 3-trimethyl ISOBEN Zofran-4-IRU)-5-chloro -1, 3-dimethyl pyrazole-4-carboxamide, N-[2 and 6-dibromo-4-(trifluoro methoxy) phenyl]-2-methyl-4-(trifluoromethyl)-5-thiazole carboxamide, 2,2-dichloro-N-[1-(4-chlorophenyl) ethyl]-3-methyl cyclopropane carboxamide, Methyl (E) -2-2-6 - (2-cyano phenoxy) Pyrimidine-4-yloxy-phenyl-3-methoxy acrylate, 5-methyl-triazolo [1, 2, and 4-] [3 and 4-b] benzothiazole, 3-allyloxy -1, 2-benzoISOCHI azole -1, 1-dioxide, diisopropyl = 1, 3-dithiolane-2-ylidene-malonate, O, and O-dipropyl O-4-methylthio phenyl phosphate etc.

[0036] Although the content of an agricultural-chemicals active principle is especially various and is specified by various formulation again neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0037] As a surface active agent, a nonionic surfactant, an anionic surface active agent, a cationic surface active agent, amphoteric surface active agents, or such mixture can be mentioned. Usually, a nonionic surfactant and/or an anionic surfactant are used. As this nonionic surfactant, specifically For example, polyoxyethylene carboxylate, The polyoxyethylene polyoxypropylene alkyl aryl ether, A polyoxyethylene polyoxypropylene block copolymer, polyvinyl alcohol, A maleic anhydride, and the copolymerization object of diisobutylene, a polyvinyl pyrrolidone, A polyoxyethylene polystyrene block copolymer, polyoxyethylene alkyl aryl ether, Polyoxyethylene alkyl ether, polyoxyethylene polyoxypropylene tris CHIRIRU phenyl ether, Polyoxyethylene styryl phenyl ether, polyoxyethylene tris CHIRIRU phenyl ether, Polyoxyethylene fatty acid ester, fatty acid ester, polyhydric-alcohol fatty acid ester, Polyoxyethylene polyhydric-alcohol fatty acid ester, polyoxyethylene alkylamine, etc. can be mentioned. As this anionic surfactant specifically For example, dialkyl sulfo carboxylate, alkylaryl sulfonates, An alkyl sulfonate, sulfo succinate, higher-fatty-acid alkali salt, A polycarboxylic acid salt, polyoxyethylene alkyl ether phosphate, Polyoxyethylene-alkyl-aryl-ether phosphoric ester, polyoxyethylene TORISUCHIRIRU phenyl ether phosphoric ester, The formalin condensate of alkylnaphthalenesulfonate and alkylnaphthalenesulfonate, a naphthalene sulfonic-acid polycondensation object metal salt, an alkenyl sulfonate, dialkyl SAKUSHI sulfonate, a ligninsulfonic acid salt, etc. can be mentioned. A surfactant is independent, or it may be used for two or more sorts by it, mixing. Although the content in an agricultural-chemicals constituent is especially various and is specified by various formulation again neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0038] As a solvent, an aromatic series solvent, a polar solvent, and animal and vegetable oils can be mentioned. As a solvent, a paraffin series solvent, an aromatic solvent, polar solvents, animal and vegetable oils, and various waxes can be mentioned. As a paraffin series solvent, normal paraffin, isoparaffin, cycloparaffin, a liquid paraffin, etc. are mentioned. As an aromatic solvent, a xylene, alkylbenzene, alkyl naphthalene, phenyl xylyl ethane, diphenyl xylyl ethane, etc. can be mentioned. As a polar solvent Cyclohexanone, heptanone, octanone, and nona non, a N-methyl-2-pyrrolidone, Ketones, such as an acetophenone, acetic-acid hexyl, benzyl acetate, phenylethyl acetate, Benzyl benzoate, methyl benzoate, oleic acid isobutyl, Benzyl salicylate, butyl-acetate cyclohexyl, methyl phenylcarbinyl acetate, Methyl oleate, methyl laurate, a dibasic acid ester with 2-4 ethylene, Diisodecyl phthalate, a dioctyl phthalate, diisodecyl adipate, Ester, such as alkylene dicarboxylic acid monochrome, such as diisobutyl adipate and adipic-acid isobutyl, or diester Ethylene glycol, propylene glycol, benzyl alcohol, Alcohols, such as phenyl ethyl alcohol, a butyl cyclohexanol, and phenyloxy ethanol, etc. can be mentioned, and oleum rapae, soybean oil, the linseed oil, etc. can be raised as animal and vegetable oils. Furthermore, the ester of a higher fatty acid or a higher fatty acid can be mentioned.

[0039] A solvent is independent or can be used as two or more sorts of mixture. It is not concerned with dosage forms, but what has the usually high flash point is good, and is 100 degrees C or more still more preferably 60 degrees C or more preferably. Although the content varies in the combination list of a solvent with dosage forms or the content purpose, it can be suitably decided to be it for the purpose, such as handling nature at the time of

pharmaceutical preparation spraying of the handling nature at the time of manufacture, the crystal deposit prevention at the time of cold storage, effect enhancement, viscosity accommodation, etc.

[0040] Although the content in the pharmaceutical preparation of a solvent is especially various and is specified by various formulation again neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0041] As a thickener, there are what is used in an oil, and a thing used underwater. As what is used in an oil, it is BENTONE, for example. SD-1 (trade name of RHEOX, Inc.), BENTONE SD-2 (trade name of RHEOX, Inc.), BENTONE SD-3 (trade name of RHEOX, Inc.), BENTONE 34 (trade name of RHEOX, Inc.) BENTONE 38 (trade name of RHEOX, Inc.), THIXATROL ST (trade name of RHEOX, Inc.), THIXATROL SR/100 (trade name of RHEOX, Inc.), THIXATROL289 (trade name of RHEOX, Inc.), THIXCIN R (trade name of RHEOX, Inc.) THIXATROL Organic clay, organic bentonite, and organic montmorillonites, such as 53X (firm RHEOX), can be mentioned.

[0042] As what is used underwater, biotechnology gums, such as water soluble polymers, such as polyoxyalkylene, polyvinyl alcohol and polycarboxylic acid carboxymethylcellulose sodium, hydroxyethyl cellulose, methyl cellulose, and its derivative, xanthan gum, UERANGAMU, guar gum, a tragacanth gum, and sodium alginate, magnesium silicate aluminum, etc. can be mentioned, for example. Although the content in these pharmaceutical preparation is especially various and is specified by various formulation again neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0043] As a defoaming agent, it is TSF, for example. 451 (trade name of Toshiba Silicone), Silicone system defoaming agents, such as TSA720 (trade name of Toshiba Silicone), and YSA02 (trade name of Toshiba Silicone), Antiform C (trade name of Dow Corning), Antiform CE (trade name of Dow Corning) TSA730 (trade name of Toshiba Silicone), TSA731 (trade name of Toshiba Silicone), Fluoro system compounds, such as a defoaming agent of a silicone system moisture powder type [, such as TSA732 (trade name of Toshiba Silicone) and YMA6509 (trade name of Toshiba Silicone),] and perfluoroalkyl phosphoric acid, etc. are mentioned.

[0044] Although the content in the pharmaceutical preparation of a defoaming agent is especially various and is specified by various formulation again neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0045] As an antifreezing agent, glycols, such as propylene glycol, a polypropylene glycol, ethylene glycol, and a diethylene glycol, are mentioned, for example. Although the content in the pharmaceutical preparation of an antifreezing agent is especially various and is specified by various formulation again neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0046] As a solid support, the mineral matter used for the usual agricultural-chemicals solid preparations and non-subtlety powder can be mentioned, and, specifically, clay, the diatom earth, talc, a calcium carbonate, an ammonium sulfate, a bentonite, a zeolite, the acid clay, the activated clay, attapulgite, an ammonium sulfate, a sodium sulfate, potassium chloride, a urea, synthetic water oxidization silicon, a carboxymethyl cellulose, etc. can be mentioned. Moreover, organic impalpable powder, such as saccharides, such as starch, a dextrin, a lactose, and cane sugar, wood flour, walnut husks, a corn cob, and powdered cellulose, is mentioned.

[0047] When it contains liquid components, such as a liquid Hara object and a solvent, especially, it is desirable as an oil absorption agent to use a wet silica also in the solid support of oil absorption nature, such as synthetic water oxidization silicon, attapulgite, a bentonite, and a zeolite. Although the content in the pharmaceutical preparation of a solid support is especially various and is specified by various formulation again neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0048] As an adjuvant, the amelioration agent of a fluidity and dispersibility or an active principle stabilizer is mentioned. Specifically, metal salt [of a higher fatty acid], talloil-fatty-acid, calcium stearate, alkyl phosphoric acid derivative, and alkali-metal way acid chloride, alkaline-earth-metal way acid chloride, etc. are mentioned. The content in the pharmaceutical preparation of an adjuvant is 70 or less % of the weight usually 10 or less % of the weight still more preferably 30 or less % of the weight preferably.

[0049] When these constituents are oils, it is obtained by mixing an agricultural-chemicals Hara object and a solvent, or adding a solvent, a surfactant, a viscosity modifier, etc. further as occasion demands, and mixing. The aforementioned thing can be used as a solvent and a surfactant. As a viscosity modifier, the solvent of hyperviscosity like animal and vegetable oils and a liquid paraffin and a thickener usable in oil are used, for example. Although the content in the pharmaceutical preparation of each component is especially various and is

specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0050] When these constituents are liquids and solutions, an agricultural-chemicals Hara object and water with the degree of aqueous solution higher than a dilution scale factor or a water-soluble solvent, and if needed, a surfactant, a stabilizing agent, a coloring agent, a defoaming agent, etc. can be mixed as a dissolution assistant, and it can manufacture by the same approach as oils. The aforementioned thing can be used as a solvent and a surfactant. Especially, in the case of liquids and solutions, the water-soluble coloring agent [like] which can identify after water dilution is mixed in many cases. Although the content in the pharmaceutical preparation of each component is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0051] When this constituent is an emulsion, it is obtained by dissolving this compound into the mixture which consists of a solvent, a surfactant, etc. As a surfactant or a solvent, although illustrated, a kind or two sorts or more of mixture can be mentioned, and although the content is not said thing especially various and specified according to a pharmaceutical preparation dilution scale factor or a spraying gestalt, it is usually as having described above.

[0052] When this constituent is suspension-among oil mold pharmaceutical preparation, it is obtained by carrying out grinding distribution of the mixture which added assistants, such as a surface active agent, and a thickener, a solvent, if needed on the agricultural-chemicals Hara object using the technique of wet grinding using media, such as a glass bead and a zirconia. Moreover, it can also obtain by distributing to homogeneity this compound beforehand ground by the dry grinding approaches, such as a hammer mill and Ayr Mill, into an agricultural-chemicals Hara object and a surfactant, and the mixture that consists of an oil absorption agent, a grinding aid, a thickener, a defoaming agent, a solvent, etc. if needed. In addition, about a thickener, it can prepare by mixing adding a thickener or its solvent dispersion liquid, and warming if needed, for example after the time of wet-grinding distribution, or grinding distribution.

[0053] Although the solvent illustrated in the first half can be mentioned as a solvent, 1% or less of thing usually has the desirable solubility of an agricultural-chemicals Hara object, for example, solvents, such as a paraffin oil and vegetable oil, are chosen in many cases. Usually, these solvents have high viscosity in many cases, and solvents, such as an aromatic series system and an ester system, may be mixed for the purpose, such as viscosity accommodation and a fall of a joining point. This solvent can also be suitably chosen from said solvents. Although the content in the pharmaceutical preparation of a solvent is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0054] As a thickener, the thickener used in said illustrated oil can be mentioned, and although the content is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0055] As a surfactant, said illustrated surfactant can be mentioned, and although the content is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above. As a defoaming agent, said illustrated thing is mentioned and an oil type and solid type thing is good especially. Although the content in pharmaceutical preparation is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0056] When this constituent is underwater suspension mold pharmaceutical preparation, it is obtained by carrying out grinding distribution of the mixture which added the surface active agent, and a thickener, water, a defoaming agent and an antifreezing agent if needed on the agricultural-chemicals solid-state Hara object of water-insoluble nature using the technique of wet grinding using media, such as a glass bead and a zirconia. Moreover, it can also obtain by distributing to homogeneity this compound beforehand ground by the dry grinding approaches, such as a hammer mill and Ayr Mill, into an agricultural-chemicals Hara object and a surfactant, and the mixture that consists of grinding aids, such as a wet silica, a thickener, a defoaming agent, an antifreezing agent, etc. if needed. In addition, about a thickener, it can prepare by mixing adding a thickener or its water dispersion and warming if needed, for example after the time of wet-grinding distribution, or grinding distribution.

[0057] Moreover, oil absorption agents, such as a wet silica, may be made to support a solvent by the case, and you may mix. The solvent illustrated as a solvent in the first half can be mentioned. As a thickener, the thickener used by underwater [said / which was illustrated] can be mentioned. Said illustrated surfactant can be mentioned as a surfactant. As a defoaming agent, said illustrated thing is mentioned and a moisture powder type thing is good especially. The aforementioned glycols are mentioned as an antifreezing agent. Although the content is especially

various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0058] When this constituent is underwater emulsion pharmaceutical preparation, water is made to distribute a solution with the solution made to dissolve an agricultural-chemicals solid-state Hara object in a hydrophobic solvent or an agricultural-chemicals liquid Hara object, and/or a hydrophobic solvent, and a surfactant, and it is obtained by adding an antifreezing agent, a thickener, a defoaming agent, etc. as occasion demands. Or a water-soluble agricultural-chemicals Hara object and a hydrophobic solvent can be reached, water can be made to be able to distribute a surface active agent with agitators, such as a homogenizer, and it can also obtain by adding an antifreezing agent and a thickener as occasion demands. Said illustrated surfactant can be mentioned as a surfactant. Water soluble polymers, such as polyvinyl alcohol and a polyoxyethylene polyoxypropylene blockpolymer, are desirable especially.

[0059] As a solvent, said aromatic series solvent and insoluble polar solvents which were illustrated are mentioned, and the content is 60 or less % of the weight usually 30 or less % of the weight still more preferably 50 or less % of the weight preferably. The aforementioned glycols are mentioned as an antifreezing agent.

[0060] What is used by underwater [said] is mentioned as a thickener, and a defoaming agent aforementioned moisture powder type is mentioned as a defoaming agent.

[0061] Although these contents are especially various and are specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, they are usually as having described above.

[0062] When this constituent is SASUPO emulsion pharmaceutical preparation, as a suspended formed element, the formed element of water-insoluble nature, such as an agricultural-chemicals Hara object, a grinding aid, a surfactant, and an effect enhancement agent, is mentioned, and liquid components, such as an agricultural-chemicals liquid Hara object, a hydrophobic solvent, and an effect enhancement agent, a hydrophobic specific gravity modifier, are mentioned as an emulsified liquid component. As a manufacturing method of this pharmaceutical preparation, the formed element of water-insoluble nature, a surfactant, and the mixture of water The suspension which carried out grinding distribution using the technique of wet grinding using media, such as a glass bead and a zirconia, is prepared. On the other hand, a liquid component and a surface active agent are added, the emulsified liquid distributed with agitators, such as a homogenizer, is prepared, this suspension and this emulsified liquid are mixed, and it is obtained by carrying out addition mixing of a thickener, an antifreezing agent, the defoaming agent, etc. if needed. Moreover, a liquid component and a surface active agent can be added, the emulsified liquid distributed with agitators, such as a homogenizer, can be prepared, and a thickener, an antifreezing agent, a defoaming agent, etc. can also be obtained addition and by carrying out homogeneity distribution to this emulsified liquid the formed element beforehand ground by the dry grinding approaches, such as a hammer mill and Ayr Mill, and if needed. Each [these] component is the same as what was illustrated with aquosity student suspension pharmaceutical preparation or underwater emulsion pharmaceutical preparation, and although the content is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0063] When this constituent is microemulsion pharmaceutical preparation, water can be added carrying out homogeneity mixing and agitating an agricultural-chemicals Hara object, a solvent, and a surfactant, and it can manufacture by the phase inversion method. It is obtained by this water solution if needed by carrying out addition mixing of a thickener, an antifreezing agent, the defoaming agent, etc. Each [these] component is the same as what was illustrated with aquosity student suspension pharmaceutical preparation or underwater emulsion pharmaceutical preparation. Furthermore, since it is a transparency water solution like the time of liquids and solutions, a water-soluble coloring agent is used for discernment in many cases. Although the content of each [these] component is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0064] When this constituent is microcapsule pharmaceutical preparation, it can usually manufacture by the approach equivalent to the manufacturing method of underwater emulsion pharmaceutical preparation or underwater suspension pharmaceutical preparation except encapsulating after producing suspension or an emulsification condition. some are mentioned as encapsulation -- having -- for example, interfacial polymerization, an emulsion-polymerization method, a suspension-polymerization method, and in-situ -- law, hardening-among liquid coating, a phase separation method, liquid drying, etc. are mentioned. Generally interfacial polymerization is adopted from the reasons of manufacture in many cases, and the water-soluble compound containing amino groups, such as a hydrophobic compound containing an isocyanate radical, water, a urea, and glycols, or a hydroxyl group is used as a polymerization nature monomer in this case. It is as could mention the same thing as said aquosity emulsion

pharmaceutical preparation as the solvent used into this pharmaceutical preparation, a thickener, an antifreezing agent, and a defoaming agent, and having also usually described the content above.

[0065] When this constituent is powder material, for example, after mixing the aforementioned solid support on an agricultural-chemicals Hara object, adding adjuvants, such as the above mentioned solvent, a stabilizing agent, a coloring agent, a surfactant, a fluid improvement agent, a drift inhibitor, and an effect enhancement agent, if needed and grinding by the hammer mill, Nara style grinder, Ayr Mill (jet O mizer etc.), etc., a solid support and an adjuvant are mixed further as occasion demands, and it can manufacture. Each of these components can mention said illustrated thing, and although the content is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0066] Generally as a drift inhibitor, solvents of high viscosity, such as machine oil, and the surfactant of a liquid are used.

[0067] When these constituents are water soluble powders, the agricultural-chemicals Hara object where the degree of aqueous solution is higher than a dilution scale factor, water-soluble solid supports, such as a saccharide, and mineral salt, an organic-acid salt, and if needed, a solvent, a surfactant or a stabilizing agent, a coloring agent, a fluid improvement agent, an effect enhancement agent, a defoaming agent, etc. are mixed as a dissolution assistant, and it can grind, mix and manufacture by the same approach as powder material. Although the water-soluble thing of the solvent used as a dissolution assistant is desirable, when dissolving in water with combination with a surfactant, the solvent of itself hydrophobicity is sufficient as it.

[0068] Although the content of each of these components is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0069] When this constituent is water dispersible powder, a solid support is mixed to an agricultural-chemicals Hara object and a surfactant, adjuvants, such as the solvent further described above if needed, a stabilizing agent, a coloring agent, a surfactant, a fluid improvement agent, an effect enhancement agent, and a defoaming agent, are added, and it grinds by the hammer mill, Nara style grinder, and Ayr Mill (jet O mizer etc.), and it mixes after that and can manufacture.

[0070] When an agricultural-chemicals Hara object is a liquid, or when it contains a solvent, it is desirable to contain the solid support of oil absorption nature, such as a wet silica. Although the content in the pharmaceutical preparation of each component is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0071] In the case of the granular pharmaceutical preparation of a granule or granulation water dispersible powder, this constituent can manufacture by the approach by the granulation, or the method of infiltrating a granulation object. The fluid bed corning method, a spray-drying-granulation method, the extrusion corning method, the rolling corning method, the compression corning method, etc. can specifically be mentioned as an approach by the granulation.

[0072] For example, the fluid bed corning method is an approach of spraying the water solution or dispersion liquid which contains a joint agent in the pulverized agricultural-chemicals solid Hara object and/or the agricultural-chemicals liquid Hara object solidified by the oil absorption agent and the fine particles which consist of a solid support, or the fine particles which added a surfactant, a solvent, lubricant, a defoaming agent, etc. as occasion demands to these fine particles as occasion demands, making fine-particles particles condensing, and drying and manufacturing the moisture after granulation. In addition, as the addition approach of a liquefied constituent, in addition to the approach of adding, for example at the time of preparation of said fine particles, the approach of adding to the direction of spray liquid, and after carrying out granulation desiccation by said approach and obtaining a granular object further, spraying mixing can be carried out and a solvent can also be obtained in this granular object.

[0073] A spray-drying-granulation method is an approach of corning by spraying the water solution or dispersion liquid which contains a solid support, a solvent, a surfactant, a joint agent, lubricant, a defoaming agent, etc. further according to the agricultural-chemicals solid Hara object pulverized, for example and/or the agricultural-chemicals liquid Hara object solidified by the oil absorption agent, and the need into hot blast, and drying moisture to coincidence. In addition, a liquefied presentation can be sprayed for the granular object which does not contain a liquefied presentation other than the approach of adding as the addition approach of a liquefied constituent, for example at the time of fine-particles preparation before the aforementioned spray drying on this granular object after manufacture by this approach.

[0074] In a knockout granulation, to them, to them, the water solution containing water or a joint agent is added to the pulverized agricultural-chemicals solid Hara object and/or the agricultural-chemicals liquid Hara object solidified by the oil absorption agent and the fine particles which consist of a solid support, or the fine particles which added a solvent and a surfactant, lubricant, and a defoaming agent further as occasion demands to these fine particles, this kneading object is extruded on a screen after kneading, it cracks by suitable die length, and it corns after drying moisture with a dryer to them. In this approach, a liquefied constituent may be mixed and manufactured in the water solution containing water or a joint agent instead of mixing in fine particles. Moreover, spraying mixing of the liquefied constituent can also be carried out at the granulation object corned and obtained, without adding a liquefied constituent.

[0075] As a solid support, in the case of a spray-drying-granulation method, it is not necessarily required, but the solid support generally illustrated in said powder material is used, and its one sort or two sorts or more can be used, for example. Although the content in the pharmaceutical preparation is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0076] As a surfactant, said illustrated surfactant can be mentioned and those one sort or two sorts or more can be used. In a granule and granularity water dispersible powder, although the content in the pharmaceutical preparation is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above. However, when manufacturing granulation water dispersible powder by the spray-drying-granulation method, the content in the pharmaceutical preparation is usually 0.1 - 95 % of the weight.

[0077] As a joint agent, a carboxymethyl cellulose, methyl cellulose, polyvinyl alcohol, a polyvinyl pyrrolidone, a dextrin, soluble starch, a ligninsulfonic acid salt, etc. are mentioned, for example. Although it is also when unnecessary [a bentonite is used as a solid support and], it is usually as having described above.

[0078] Said illustrated solvent can be mentioned as a solvent or a defoaming agent.

[0079] As lubricant, the thing which made oil absorption agents, such as a silica, support the wax-like matter or the high viscosity oil of a lubricating oil, and it can be mentioned. As wax-like matter, a capric acid, a lauric acid, stearin acid, Usual [, such as oleic acid,] A with a carbon numbers of ten or more fatty acid, calcium stearate, Magnesium stearate, a sodium stearate, zinc stearate, As fatty-acid metal salts, such as aluminum stearate and barium stearate, powdered paraffin, wax various kinds, and liquefied matter Usual [, such as a caproic acid, a caprylic acid, and pelargonic acid,] can mention fluid material, such as higher alcohol, such as a fatty acid of carbon numbers 6-9, oleyl alcohol, and stearyl alcohol, a liquid paraffin, a naphthene, silicone oil, and its derivative.

[0080] In the case of a dry type granulation, the pulverized agricultural-chemicals solid Hara object and/or the agricultural-chemicals liquid Hara object solidified by the oil absorption agent and the fine particles which consist of a solid support, or the fine particles which added a solvent and a surfactant, lubricant, the joint agent, and the defoaming agent further as occasion demands to these fine particles is pressed with a roller compactor etc., and after that, it carries out a crack screen exception and is obtained. As a solid support in this case, saccharides, such as a lactose, are used in many cases.

[0081] In the case of granulation water dispersible powder, disintegrator may contain further if needed. As disintegrator, in the case of the matter swollen in underwater [, such as carboxymethyl-cellulose calcium a bridge formation object of a polyvinyl pyrrolidone, and xanthan gum,], or a dry type granulation article, it reacts by underwater [like the mixture of carbonates, such as solid acid, such as a maleic anhydride, and a sodium hydrogencarbonate,], and what generates and emits a carbon dioxide is mentioned. Although the content in these pharmaceutical preparation is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0082] In the case of a granule, the approach of infiltrating a granulation object can be manufactured by making the solution which adds a surface active agent and a coating agent further as occasion demands to the solution or suspension prepared from for example, an agricultural-chemicals Hara object and a solvent, and is prepared by the granular support of the porosity of a pumice powder broken kernel, a bentonite grinding grain, a vermiculite grinding grain, a pearlite grinding grain, various baking grains, etc. support. Furthermore, the case of a granule and granulation water dispersible powder can also be considered as granular pharmaceutical preparation by making the granular support which corned by the various granulation approaches support the solution or suspension prepared from an agricultural-chemicals Hara object and a solvent. This granular support is usually contained 30 to 95% of the weight in pharmaceutical preparation. Moreover, the content of a solvent is about 50 % of the weight.

[0083] When manufacturing a tablet, a surfactant, a solvent, a joint agent, disintegrator, etc. are mixed as occasion demands to the pulverized agricultural-chemicals solid Hara object and/or the agricultural-chemicals liquid Hara object solidified by the oil absorption agent and the fine particles which consist of a solid support, or these fine particles, and it fabricates with a tableting machine in predetermined magnitude and form. Although the above mentioned thing is mentioned as a solid support, saccharides, such as a lactose, are used in many cases. Each other presentations are almost equivalent to the aforementioned granule, and although the content in pharmaceutical preparation is especially various and is specified neither according to a pharmaceutical preparation dilution scale factor nor a spraying gestalt, it is usually as having described above.

[0084] This constituent pharmaceutical-preparation-ized by various gestalten is used for prevention of a noxious organism, accommodation of vegetable growth, etc. As an application ground, it is applicable to processing in others, land under perennial crops, a pasture, the grass ground, the forestry ground or a channel, a canal, or other non-crop land etc. [crop land /, such as fields,] Although it may change by a meteorological condition, formulation, a processing stage, the art, soil conditions, object crops, and object weeds when carrying out spraying processing of this constituent, all the gestalten sprinkled by the usual agricultural chemicals as the use approach can be taken. For example, it can sprinkle directly to a spraying location, a seedling box, etc. of fields or non-crop land, or the approach of using it for crops, soil, etc. with a paint gun etc. can be mentioned after diluting in water. Although the dilution scale factor to water is based also on the class of agricultural-chemicals active principle in this agent, or the class and use scene of a content and an object noxious organism, usual is about 500 to 4000 times still more preferably about 50 to 8000 times preferably about 10 to 10000 times.

[0085] Also as the approach of a paint gun, it carries on the back, and aerial applications, such as ground applications, such as a formula paint gun and a boom sprayer, a radio control helicopter, a HEL, and a Cessna, occur.

[0086] As a package gestalt of this pharmaceutical preparation, an usable container can be used with the usual agricultural-chemicals pharmaceutical preparation. For example, in the case of liquids and solutions, PURABOTORU by which coating was carried out to the monolayer or the double layer, a Tin can, an iron can, KEMIDORAMU, a 1-to size container, Raleigh, etc. are mentioned, and when it is a solid preparation, an aluminum bag, a paper bag, a paper pack, a water soluble film, etc. are mentioned. In order to avoid the moisture absorption at the time of preservation, a paper bag, a plastic bag, etc. with which aluminum coating of an aluminum bag or the interior was carried out are desirable. Moreover, the moisture absorption prevention at the time of preservation, improvement in safety, improvement in the usability at the time of dilution, etc. are expectable by filling up these bags with what was packed up in the water-soluble pack.

[0087] This pharmaceutical preparation may contain other herbicides, an insecticide, miticide, a nematocide, a germicide, a plant growth regulator, an insect growth regulator, fertilizer, the soil conditioner, the synergist, the adjuvant, etc. as occasion demands further.

[0088]

[Effect of the Invention] According to this invention, when silica support has the above-mentioned characteristic value, water-dispersion is high, and since it is hard to condense, the solid preparations excellent in the preservation stability of a fines agent and the granulation water dispersible powder excellent in collapsibility can be offered.

[0089]

[Example] Although an example and the example of a comparison are shown and this invention is explained concretely hereafter, this invention is not restricted to the following example.

[0090] [Example 1] silicic-acid concentration warmed No. 3 sodium-silicate water-solution 100L which is 5 w/v% at 95 degrees C, and added sulfuric-acid 2.5L of 12 normality under stirring. Next, it stirred for 30 minutes and 2.2L addition of the sulfuric acid of 12 normality was done. It heated for 30 more minutes. After adjusting pH to 4.0, the slurry was filtered and washed and it re-distributed in water. After adjusting pH to 4.0, the slurry was filtered and washed and the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification.

[0091] [Example 2] silicic-acid concentration warmed No. 3 sodium-silicate water-solution 100L which is 5 w/v% at 95 degrees C, and added sulfuric-acid 2.5L of 12 normality under stirring. Next, it stirred for 30 minutes and 2.2L addition of the sulfuric acid of 12 normality was done. It heated for 30 more minutes. After adjusting pH to 7.0, the slurry was filtered and washed and it re-distributed in water. After adjusting pH to 8.5, the slurry was filtered and washed and the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification.

[0092] The [example 1 of comparison] silicic-acid concentration warmed No. 3 sodium-silicate water-solution 100L which is 7 w/v% at 90 degrees C, and added sulfuric-acid 2.7L of 12 normality under stirring. Next, it stirred for 30 minutes and 3.9L addition of the sulfuric acid of 12 normality was done. It heated for 30 more minutes. This slurry was filtered and washed and it re-distributed in water. This slurry was filtered and washed and the silica of a predetermined grain size was further obtained by desiccation, grinding, and the classification.

[0093] The burned product of a wet silica was obtained by heat-treating the silica obtained in the example 1 of the [example 2 of comparison] comparison at 900 degrees C for 1 hour. The physical properties of the silica obtained in the top are shown in Table 1. In addition, the physical-properties measuring method is as follows. Moreover, a pore distribution curve is shown in drawing 1 R> 1.

[0094] With the Coulter counter MS-II mold particle-size-analysis machine made from [Mean-particle-diameter] Beckmann Coal tar, particle size distribution were measured using the aperture (100 micrometers or 30 micrometers), and the median size (50% particle size) was made into mean particle diameter.

[0095] Using the full automatic gas adsorption equipment BELSORP28 made from [pore Distribution] Japan Bell, it asked for the nitrogen adsorption isotherm in liquid nitrogen temperature, the analysis method of a DORIMOA heel was applied to the obtained desorption constant-temperature line based on JIS-K1150, and pore distribution (Rp vs. dVp/dRp) was searched for. In addition, pretreatment of a sample carried out degassing for 90 minutes at 160 degrees C.

[0096] It is the pore radius for which it asked from the pore distribution map of each sample shown in [pore peak radius] drawing 1 and which shows the maximum of dVp/dRp.

[0097] The oil absorbed amount per silica 100g about dibutyl phthalate (DBP) oil was made into oil absorption using the automatic oil absorption measuring device made from [Oil absorption] Chlorofluocarbon Tex.

[0098]
[Table 2]

	実施例 1	実施例 2	比較例 1	比較例 2
平均粒子径 (μm)	8.0	7.9	8.1	4.6
細孔ピーク半径 (nm)	12	12	不明確	不明確
dVp/dRpの最大値 ($\text{mm}^3/\text{nm}\cdot\text{g}$)	150	150	40	30
吸油量 (mL/100g)	220	214	251	241

[0099] Next, granulation water dispersible powder was prepared by the formula shown in Table 3 using the above-mentioned silica.

[0100]
[Table 3]

種類	量	固形分割合
液体原体	40.0 g	38%
シリカ (担体)	42.0 g	40%
界面活性剤	18.0 g	17%
クレー (増量剤)	5.0 g	5%

[0101] After mixing a liquid Hara object with a silica in a mortar beforehand, grinding mixing of this was carried out. A surfactant and clay were added after that and it mixed. Water is added so that it may become a moderate moisture content, this is extruded and it granulates by 0.8mm of **** by the corning method, and after arranging the

grained die length, it was made to dry for 45 minutes at 60 degrees C. A part for a sieve part opium poppy, a coarse-grained fraction, and a particle was removed by 1180 micrometers of ****, and the 800-micrometer screen.

[0102] It measured about underwater collapsibility, self-diffusion nature, and dispersibility by the following approach about the obtained granulation water dispersible powder. A result is shown in Table 4.

[0103] 1.0g of granulation prepared to the Nessler tubes into which underwater collapsibility 3 degree hard water 50mL was put was added, and it was made to fall up and down. It considered as underwater collapsibility with the count of a fall taken for a particle to disappear.

[0104] At the time of self-diffusion nature underwater collapsibility measurement, 1 or 2 grains of granulation was put in into 3 times hard water, and the collapsibility of the grain at the time of a grain reaching by the tube bottom was judged by viewing.

[0105] The liquid completely distributed after dispersibility underwater collapsibility measurement is put for 10 minutes. It considered as dispersibility with the volume which sedimented.

[0106]

[Table 4]

	水中崩壊性	自己拡散性	分散性	総合評価
実施例 1	10 回	△	0.10mL	非常に良い
実施例 2	15 回	△	0.15mL	非常に良い
比較例 1	40 回	△	2.0mL	悪い
比較例 2	30 回	△	1.5mL	悪い

[0107] As compared with the example 2 of a comparison using the burned product of a wet silica with which the conventional example 1 of a comparison and the dispersibility using a sedimentation nature silica are made good by the above-mentioned result, the examples 1 and 2 using the silica by this invention are understood that underwater collapsibility and dispersibility are very good. therefore, the silica of this invention which is a gel type silica -- agricultural-chemicals liquid Hara -- the body and its function -- by using as a carrier showed that the good granulation water dispersible powder of the collapsibility which was not obtained was obtained in a conventional sedimentation nature silica and a conventional baking silica.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the pore distribution curve of the silica of an example and the example of a comparison.

Drawing 1:

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